

PATENT SPECIFICATION

(11) 1244 101

NO DRAWINGS

- (21) Application No. 3882/69 (22) Filed 23 Jan. 1969
 (31) Convention Application No. 700373 (32) Filed 25 Jan. 1968 in
 (33) United States of America (US)
 (45) Complete Specification published 25 Aug. 1971
 (51) International Classification C 23 c 3/02
 (52) Index at acceptance

C7F 1A 1B1B 2G 2L 2N 2P 2U 2V 4J 4M 4N
 H1H 1 3E 6A 6B 8B

- (72) Inventors MELVIN DAVID STERMAN and
 DAVID JOSEPH GENOVA



(54) METALLISING A SUBSTRATE

- (71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a process for forming on a surface of a substrate, such as plastic tape, a uniform layer of a noble metal, and to a process wherein said noble metal layer is then utilized as a catalytic layer for use in the electroless deposition of a ferromagnetic layer on said substrate for use as a magnetic record member.
- Processes for forming metallic coatings by electroless deposition on a substrate, for various purposes, have been known, and in fact this general technique has been disclosed for use in the production of magnetic record members. See for example Canadian Patent 705,366 (U.K. specn. 992,660) which discloses sensitizing a tape support by passing it through a bath containing a reducing agent such as stannous chloride or titanous chloride to leave a residue thereof on the tape, then passing it through a "seeding" solution containing palladium chloride, which reacts with the stannous or titanium chloride to form particles of metallic palladium on the surface of the tape. The "seeded" tape is then passed through a bath containing various cobalt, nickel and phosphorus-containing salts which are catalytically reduced by the palladium to form the final magnetic recording surface.
- While quite effective record members can be made in this way it has been found extremely difficult to obtain that degree of uniformity of magnetic characteristics which is essential for high quality magnetic tapes. We have found that this problem arises primarily due to uneven distribution of the particles of catalytic metal, e.g. palladium, on the substrate prior to deposition of the magnetic material. This unevenness appears to be caused by a combination of two factors: the difficulty of obtaining a truly uniform coating of any material merely by dipping techniques, and a tendency for stannous and titanium chloride particles to agglomerate, as evidenced by a somewhat mottled appearance of a tape coated therewith, whether by dipping or by some other coating technique. This known process also has the objection that the substrate will be coated on both sides whereas it is normally desired to have the magnetic layer on but one face of a record member.
- It is therefore an object of this invention to provide a process for use in the production of magnetic records by electroless deposition techniques that will overcome these problems.
- We have found, surprisingly, that by forming the catalytic noble metal layer by employing the substantially unrelated compound, cuprous iodide, which is not normally classified as a reducing agent, instead of the prior art chloride reducing agents previously utilized, these problems are effectively overcome. Moreover when thus using cuprous iodide, conventional high-precision coating technique such as are used in manufacture of photographic film materials can conveniently be used to produce a catalytic layer of extremely fine particles of palladium or other noble metal uniformly distributed over the desired surface only of the substrate. The improvement appears in part at least to be caused by the fact that the particles of noble metal produced as a result of reaction with cuprous iodide tend to be much smaller and more uniform in size than when the prior art chloride reducing agents are used. While preferably the cuprous iodide is first applied to the substrate surface and then the noble metal salt applied thereto for reaction in situ, some of the advantages of our invention are still retained even when the cuprous iodide and noble metal salt are reacted together to

[Price 25p]

produce the noble metal particles prior to application thereof to the substrate.

5 According to the present invention there is provided a substrate having a layer thereon containing a noble metal, said noble metal having been formed by reduction of a salt of the noble metal by cuprous iodide.

10 According to the present invention there is further provided a process for forming a layer containing a noble metal on a substrate which comprises reacting cuprous iodide with a salt of the noble metal and then forming a layer containing the reaction products on the substrate or which comprises forming a layer containing the cuprous iodide on the substrate and reacting the cuprous iodide *in situ* in the layer with a salt of the noble metal.

15 According to the present invention there is also provided a method of producing a ferromagnetic layer which comprises contacting a solution of a compound of a ferromagnetic element and a reducing agent for the compound with a layer made according to the invention at a temperature at which the reduction of said compound to the ferromagnetic element is catalysed by the noble metal in said layer.

20 Thus, in the preferred embodiment of our invention, cuprous iodide is first deposited, with or without a binder, as a uniform layer on a suitable substrate such as paper or plastic sheet or tape material. When the cuprous iodide layer is dry, the noble metal salt is brought into contact with the cuprous iodide layer as by progressively traversing the substrate through a liquid bath of the noble metal salt, advantageously an aqueous solution thereof. Then the coated substrate is washed thoroughly with water to remove undesired reactants such as copper chloride or other salts that may be present, and, upon drying, the substrate will be found to have an extremely uniform, thin layer of the noble metal thereon in a state suitable to act as a catalyst for the subsequent deposition of a ferromagnetic metal on the substrate.

25 In a second embodiment for preparing a noble metal layer on the substrate in accordance with our invention, a dispersion of the noble metal in a liquid medium containing a binder is first prepared by mixing together the cuprous iodide, the noble metal salt, and the binder with the necessary liquid ingredients, thereby forming a dispersion of fine metal particles which is then coated onto the surface of the support and dried thereon by heating at an elevated temperature.

30 Regardless of which method is employed for producing the uniform noble metal coating, the deposition of another metal such as a ferromagnetic metal as a layer on the substrate is accomplished by bringing into contact with the noble metal layer a preferably aqueous solution of a reducing agent and a compound of the ferromagnetic metal. The ferromagnetic

metal compound should, of course, be one which is relatively readily reduced in the presence of the noble metal, thereby forming a ferromagnetic layer on the substrate. For example, the ferromagnetic metal can be cobalt, nickel, iron, or alloys of two or more of these metals with one another; and the compound which is reduced can be any suitable salt such as cobalt chloride hexahydrate.

The following Examples are examples of the invention.

EXAMPLE I

A poly(ethylene terephthalate) film support subcoated with a terpolymer composed of methyl acrylate, vinylidene chloride and itaconic acid is overcoated on one side by spreading on the subcoat a solution containing 3% by weight of cuprous iodide and 0.5% of a poly(vinyl formal) binder containing 5 to 7 mole % of vinyl alcohol and 20 to 27 mole % of vinyl acetate residues, dissolved in acetonitrile. Upon drying, the coating is found to be extremely smooth and uniform and to contain 10 mg. of cuprous iodide per square foot of substrate.

The coated substrate is next immersed for two minutes in a bath of an aqueous solution containing 0.5 g/l (grams per liter) of palladium chloride and 0.06 mole/l of hydrochloric acid (for dissolving the palladium chloride), Upon removal from the solution the coated substrate is thoroughly rinsed with distilled water and that side of the substrate which carries the cuprous iodide is found to have a correspondingly smooth, uniform layer of palladium metal thereon.

The palladium-coated substrate is next immersed for twenty minutes in an aqueous solution containing 0.03 mole/l of cobalt chloride hexahydrate, 0.06 mole/l of sodium hypophosphite monohydrate (a reducing agent), 0.23 mole/l of ammonium chloride, and 0.09 mole/l of sodium citrate dihydrate (a complexing and solubilizing agent), the solution being at a temperature of 90°C. and having a pH of 9, maintained with ammonium hydroxide.

A continuous, coherent coating of cobalt (alloyed with a small amount of phosphorus derived from breakdown of the reducing agent) is obtained, with a coverage of 550 mg. of cobalt per square foot of substrate. The cobalt-phosphorus coating is then washed in distilled water and air-dried. The dried coating is found to be extremely smooth and uniform and to be firmly bonded to the substrate; it cannot be readily rubbed, abraded, or scratched off, nor can it be pulled off with adhesive tape. The magnetic, audio and digital properties of the resulting tape are measured and found to be well adapted for both digital data storage and sound transcription. The data show that this tape has higher coercivity, better "squareness", and better frequency response charac-

teristics than conventional magnetic iron oxide tapes, and superior characteristics for digital uses. Furthermore, the required thickness of the cobalt coating for equivalency to magnetic iron oxide tapes is between 1/10 and 1/20 that of an iron oxide coating. Both the print-through and wear properties of the cobalt tape are superior to those of magnetic iron oxide tape.

EXAMPLE II

A coating dispersion of cuprous iodide in a water-soluble polymer binder is prepared using 65 ml. of an aqueous solution containing 1.55% by weight of sodium salt of a resinous carboxy ester lactone (see U.S. patent 3,169,946, U.K. specification 1,013,179) at a pH of 7, to which is added, while stirring in a suitable mixer, 35 ml. of a solution of 3% by weight of cuprous iodide in acetonitrile. 1 ml. of an aqueous solution containing 5% by weight of hexa[1-aziridine]triphosphatriazine is added just prior to the coating operation to function as a cross-linking agent for the binder. The resulting dispersion is coated on several poly(ethylene terephthalate) film substrates, some having subcoatings of the terpolymer of Example I and some having gelatin subcoatings, as well as on a cellulose acetate substrate.

After drying these cuprous iodide dispersion coatings, each of the coated substrates is dipped for two minutes into an aqueous solution containing 0.5 g/l of palladium chloride and 0.06 mole/l of hydrochloric acid, the solution being at a temperature of 60°C.

Each of the coated substrates is then thoroughly rinsed with distilled water, after which a cobalt-phosphorus layer is deposited on the palladium layer following the procedure described in Example I to give a magnetic tape having the superior properties described in Example I.

EXAMPLE III

A dispersion of fine particles of palladium metal is prepared in association with a water soluble polymeric binder by first preparing 65 ml. of an aqueous solution containing 1 g. of poly(vinyl alcohol), 0.25 g. of palladium chloride, and 0.03 mole of hydrochloric acid in a suitable mixer. To this solution is added, with continuous mixing, 35 ml. of an acetonitrile solution containing 0.6 g. of cuprous iodide to react with the palladium chloride and form the dispersion of fine particles of palladium metal. Then 1 ml. of a 10% by weight aqueous glyoxal solution is added to the dispersion to function as a crosslinking agent for the poly(vinyl alcohol), and the dispersion is promptly coated on poly(ethylene terephthalate) substrates subbed as described in Example II, as well as on cellulose acetate substrates, and dried by heating the coating. Then a cobalt-phosphorus layer is deposited on the substrates as described in connection with Ex-

ample I to produce magnetic tapes having superior properties comparable to those of Example I.

EXAMPLE IV

A coating solution containing (by weight) 1% cuprous iodide, 2.5% of poly(methyl acrylate-vinyl chloride-acrylic acid (50:46:4)), as a binder, and 2.5% trimethyl phosphite, as a solubilizing agent, is prepared in a 9:1 (parts by weight) solvent mixture of methyl ethyl ketone and cyclohexanone. The resulting solution is coated onto one side of a poly(ethylene terephthalate) film support and dried by blowing hot air over the support to yield a dry coverage of approximately 10 mg. of cuprous iodide per square foot of coating.

The cuprous-iodide-coated element is dipped for two minutes into an aqueous solution maintained at 80°C. containing 0.5 g/l of palladium chloride and 0.06 mole/l of hydrochloric acid. The element is removed from the bath, rinsed thoroughly with distilled water, and found to have a uniform, smooth catalytic layer of palladium nuclei on the coated side of the support.

The support with its layer of palladium catalytic nuclei is next immersed in an aqueous solution maintained at a temperature of 95°C. and a pH of 10.5, containing 0.03 mole/l of cobaltous chloride hexahydrate, 0.07 mole/l of sodium hypophosphite monohydrate, and 0.15 mole/l of aspartic acid. After five minutes immersion time, a continuous, uniform coating of cobalt alloyed with phosphorus has formed on the side of the support containing the catalytic nuclei.

Thorough rinsing with distilled water provides a magnetic tape element which, again, exhibits good adhesion and magnetic properties.

EXAMPLE V

A coating solution containing, by weight, 1% cuprous iodide, 2.5% DuPont Polyester Adhesive # 49,000 (a tough, hard, amber-colored, non-tacky polyester having an average specific gravity of 1.33 and an average melting range of 245-275°F.), and 2.5% trimethyl phosphite is prepared in a 1:1 (parts by weight) solvent mixture of methylene chloride and ethylene chloride. This solution is coated onto one side of a poly(ethylene terephthalate) film base and dried by blowing hot air over the support. The coating is treated as in Example IV with a palladium chloride solution, and then with a cobaltous chloride hexahydrate solution. A magnetic element is thus produced having good adhesion of a continuous, uniform cobalt-phosphorus metallic layer displaying good magnetic properties.

While the invention has been illustrated above by means of specific examples, it is evident that certain variations in the process can be employed within the scope of the invention. Thus, the cuprous iodide coverage can

be varied over a wide range and still react with sufficient palladium to provide an effective catalytic layer; for example, it can be as low as 2 mg. per square foot, although 10 mg. per square foot is advantageous for economy and efficiency. Variations in the coverage may be secured by either reducing or increasing the wet coverage of the cuprous iodide coating solution of a given concentration applied to the substrate, or by varying the cuprous iodide concentration of the coating solution while maintaining the wet coverage at a constant value. The cuprous iodide can be in aqueous solution, or in a non-aqueous solvent such as acetonitrile or propionitrile. Cuprous iodide advantageously is present in the solution in an amount between 0.005 and 5%, preferably between 1.0 and 3.0% by weight; and when a film-forming binder is used the latter can be present in an amount between 0.1 and 5%, preferably between 0.4 and 2.5%.

The concentration of the noble metal salt solution can also be varied considerably while still producing a satisfactory layer. Instead of the hydrochloric acid, other solubilizing agents such as alkali metal halides or ammonium chloride may be used to dissolve the noble metal salt initially. Furthermore, the temperature of the noble metal salt bath may be varied over a wide range, such as 20° to 98°C., with the rapidity of the reaction increasing as the temperature is increased, 60° to 98°C. giving particularly good results. A more uniform layer of noble metal results from the higher temperatures. While the noble metal is perhaps most conveniently palladium, other noble metals such as gold or platinum, can be used. Moreover, while the chlorides are convenient salts to be used, other noble metal salts can obviously be utilized. Complex salts such as platinum or palladium hydrogen chloride and palladium or platinum potassium chloride, may likewise be used.

The conditions under which the ferromagnetic metal reduction is carried out can also be varied. Advantageously, but not necessarily, the temperature of the plating solution should be between 80° and 99°C., preferably between 90° and 99°C., and the pH of the solution between 8 and 11, preferably 9 or above. There is also considerable latitude in the composition of the bath, with the cobalt chloride hexahydrate composition concentration advantageously being between 0.005 and 0.12 mole/l, preferably between 0.02 and 0.06, most desirably about 0.03 mole/l. The sodium hypophosphite monohydrate reducing agent concentration may be varied from 0.005 to 0.24 mole/l, preferably between 0.04 and 0.14 mole/liter, most desirably about 0.07 mole/liter; the ammonium chloride concentration from 0.04 to 1.0 mole/l, preferably between 0.10 and 1.0 mole/liter, most desirably about 0.23 mole/liter; and the sodium citrate dihydrate complexing and solubilizing agent concentration

from 0.03 to 0.20 mole/l, preferably between .05 and 0.15 mole/liter, most desirably about 0.09 mole/liter.

In this invention it is desirable, although not necessary, to use a binder to improve adhesion when applying the cuprous iodide layer to the support. Polymers soluble in organic solvents, including vinyl polymers and polyesters, are well adapted for this purpose; for example, polymers of vinylidene chloride, acrylic esters, and itaconic acid; vinylidene chloride and acrylonitrile; vinyl chloride and vinyl acetate; butadiene and acrylonitrile; and poly(vinyl formals). Alternatively polyesters such as those derived from poly(methylene glycols) and terephthalic acid may be employed. Examples of useful polyesters are the 'Vitel' (registered trade mark) resins sold by Good-year Tire and Rubber Company and the Dupont Polyester Adhesives 49,000, 49,001, 49,002 and 49,003.

In addition, water-soluble polymers such as poly(vinyl alcohols) and the sodium salts of resinous carboxy ester-lactones may be used.

Organic solvents which are useful in these binder formulations are acetonitrile, propionitrile, the ketone solvents, e.g., methyl ethyl ketone, halogenated solvents, and mixtures of ketone solvents, alcohols, and halogenated solvents such as methyl ethyl ketone and acetone, methyl ethyl ketone and ethyl alcohol, methyl ethyl ketone and methyl isobutyl ketone, methyl ethyl ketone and tetrachloroethane, and methylene chloride and ethylene chloride.

When a binder solution comprising an organic solvent is used, it is advantageous to employ a solubilizing agent for the cuprous iodide. Examples of such agents are trimethyl phosphite, diethyl sulfide and amines, e.g., triethylamine and trimethylamine. In certain cases (e.g. where acetonitrile or propionitrile is used as the solvent) no additional solubilizing agent is needed since the cuprous iodide is sufficiently soluble therein without such agent.

The magnetic recording elements of this invention can be further improved by the use of an adhesive subbing composition. Particularly useful for this purpose are polymers of vinylidene chloride, acrylic esters and itaconic acid; vinylidene chloride and acrylonitrile, poly(methylene glycols) and terephthalic acid, vinyl chloride and vinyl acetate, butadiene and acrylonitrile.

WHAT WE CLAIM IS:—

1. A substrate having thereon a layer containing a noble metal, said noble metal having been formed by reduction of a salt of the noble metal by cuprous iodide.

2. A process for producing a layer containing a noble metal on a substrate which comprises reacting cuprous iodide with a salt of the noble metal and then forming a layer containing the reaction products on the sub-

strate or which comprises forming a layer containing the cuprous iodide on the substrate and reacting the cuprous iodide *in situ* in the layer with a salt of the noble metal.

5 3. A process according to claim 2, in which the cuprous iodide is reacted with the salt of the noble metal in solution in the presence of a binder for the reaction products and in which a layer of the resulting liquid composition is formed on the substrate and dried.

10 4. A process according to claim 3, in which a crosslinking agent for the binder is added to said composition before forming the layer.

15 5. A process according to claim 2 in which the layer containing the cuprous iodide formed on the substrate also contains a binder for the cuprous iodide.

20 6. A process according to claim 5 in which the layer is formed with a cross-linking agent for the binder incorporated therein.

7. A process according to claim 2, 5 or 6, in which the cuprous iodide in the layer on the substrate is caused to react with the salt of the noble metal by contacting the layer with an aqueous solution of the salt at a temperature from 60 to 98°C.

25 8. A process according to any of claims 2 to 7 in which the substrate is composed of polyethylene terephthalate, cellulose triacetate or paper.

30 9. A process according to any of claims 2 to 7 in which the substrate is a sub-layer carried by a support.

35 10. A process according to any of claims 2 to 8 in which the substrate is in the form of a tape or sheet.

11. A process according to claim 9 in which the support is in the form of a tape or sheet.

40 12. A process according to any of claims 2 to 11 in which the noble metal salt is a halide.

13. A process according to any of claims 2 to 12 in which the noble metal is palladium.

45 14. A process according to any of claims 2 to 13 in which the layer containing the noble metal is washed after formation thereof to remove soluble salts therefrom.

15. A layer containing a noble metal which has been produced by a method according to any of claims 2 to 14.

16. A method of producing a ferromagnetic layer which comprises contacting a solution of a compound of a ferromagnetic element and a reducing agent for the compound with a layer according to claim 1 or 14 at a temperature at which the reduction of said compound to the ferromagnetic element is catalysed by the noble metal in said layer.

17. A method according to claim 16 in which said contacting is effected at a temperature from 90° to 99°C.

18. A method according to any of claims 16 or 17, said ferromagnetic element being cobalt.

19. A method according to claim 18 in which the reducing agent is a phosphorus-containing reducing agent.

20. A method according to claim 19 in which the reducing agent is sodium hypophosphite.

21. A method of producing a ferromagnetic layer which comprises contacting a solution of a salt of cobalt and a reducing agent for the salt with a layer which has been made by a process according to claim 13 at a temperature at which said cobalt salt is catalytically reduced by the palladium in said layer.

22. A method according to claim 21, the cobalt salt being cobalt chloride and the reducing agent being sodium hypophosphite.

23. A method according to claim 22, the concentration of cobalt chloride hexahydrate being from 0.02 to 0.06 moles per litre and the concentration of sodium hypophosphite monohydrate being from 0.04 to 0.14 moles per litre.

24. A method according to claim 23 in which said solution contains sodium citrate.

25. A method of producing a ferromagnetic layer according to claim 16 substantially as herein described.

26. A sheet or tape material comprising a ferromagnetic layer which has been produced by a process according to any of claims 16 to 25.

L. A. TRANGMAR, B.Sc., C.P.A.
Agent for the Applicants.

Printed for Her Majesty's Stationary Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.